Nanoscale Catalysis

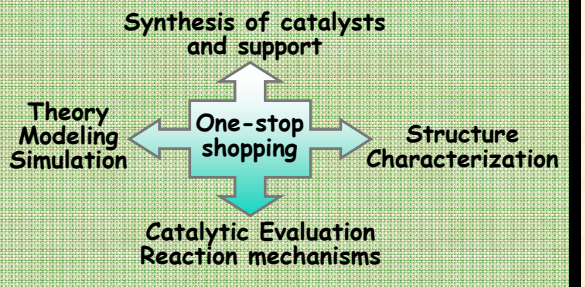
CNMS Oak Ridge National Laboratory — Center for Nanophase Materials Sciences

Office of Science — U.S. Department of Energy — Office of Basic Energy Sciences — Serving the Present, Shaping the Future

Catalysis at the CNMS - Catalytic function by design of tailored nanostructure materials -

Grand Challenges in Nanocatalysis

- Difficulty to control catalytic particle size, pore size, support structure, and uniformity
- Theory modeling and simulation to predict correlation between structure and function and electronic properties of nanoparticles
- Identification of the active site in catalytic reactions
- Structure and composition changes under reaction conditions create challenges in characterization of active sites: image catalysts at practical *in operando* conditions
- Design nanomaterials that mimic the function of homogeneous catalysts



Lab Facilities

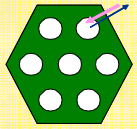
Contact: Steve Overbury (overburysh@ornl.gov)
Sheng Dai (dais@ornl.gov)
Viviane Schwartz (schwartzv@ornl.gov)
Mike Simonson (simonsonim@ornl.gov)

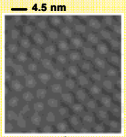
- 2 Catalysis synthesis Labs: Synthesis of nanoporous support, layer-by-layer functionalization, atomic layer deposition, etc
- Lab for catalyst characterization and reactivity: Equipment for structure characterization and in situ reaction mechanisms
- Lab for catalyst characterization and neutron scattering: More equipment for reactivity studies, material characterization and in-situ reaction cell for neutron studies
- Lab for nanoscale solvothermal synthesis processes: Synthesis of nanoparticles based on processes promoted by solvents at elevated temperatures and pressures

Synthesis of Catalysts and Supports

Synthesis of Nanoporous Support

Contact: Sheng Dai (dais@ornl.gov)





TEM Image of Nanopores

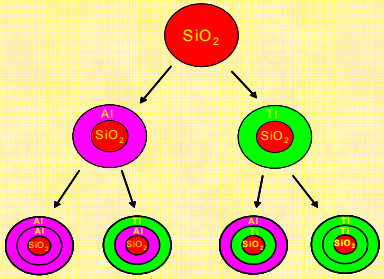
- Ion exchangeable
  various noble and transition metals possible
  walls can be functionalized
- Produce monodispersed catalyst particles
  pore size and loading to produce a single size particle
  synthesis allows variation of particle size
- High stability
- Constrained within "nanoflask"
  inhibit sintering
  control reaction products
  leads to altered selectivity

Layer-by-Layer Functionalization

catalyst supports prepared by surface sol-gel approach:

"activate" silica

- Sequential layer growth on amorphous nanoparticles of non-porous SiO2 (Cabo-Sil)
- Surface sol-gel approach or ALD
- Can use Ti, Zr, Al, Ge…
- D-P to put Au onto functionalized support
- Layer growth in pores or external surface

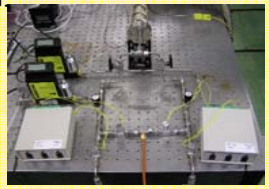


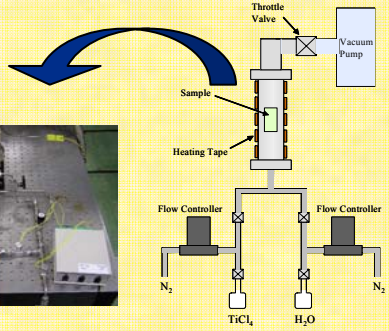
Atomic Layer Deposition

- Gas phase technique
- Excellent stability, high conformality, and reproducibility.
- Simple and accurate thickness control
- Growth is self-limiting

Preparation Procedure

- Exposure of precursor (e.g., TiCl4)
- Purge chamber
- Exposure of H2O
- Purge chamber

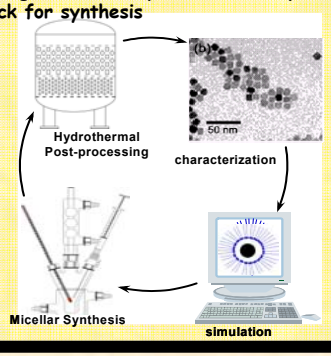




Solvothermal Synthesis of Refractory Metal Oxide nanoparticles

Contact: David Wesolowski (wesolowskid@ornl.gov)
Adam Rondinone (rondinoneaj@ornl.gov)

- Synthesize amorphous particles in organic solvents using micellar "nanoreactors"
- Crystallize particles under mild hydrothermal conditions (250 to 350C) to prevent aggregation/growth
- Characterize and monitor particle nucleation, crystallization using HRTEM, SANS, etc
- Simulate growth and crystallization to provide feedback for synthesis



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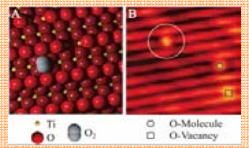
Pool of Equipment – Nanocatalysis at CNMS

- Atomic layer deposition (ALD) for conformal functionalization of support surfaces
- NMR solid/liquid
- UV-visible spectroscopy
- Fluorescence spectroscopy (Spex Fluorolog 2)
- FTIR analysis; photoacoustic detection, DRIFTS, transmission, gas environment control
- Raman spectroscopy/microscopy with environmental control
- Composition analysis - Ion coupled plasma- emission detection
- Volumetric gas adsorption; BET, surface area and pore size distribution using nitrogen.
- Volumetric specific gas adsorption; metal surface area
- Powder XRD; temperature control (LN to 900 °C), controlled gas atmosphere.
- Microscopy; SEM, bright field TEM, darkfield (Z-contrast) STEM aberration corrected Z-STEM (through ShaRe and HTML)
- Thermogravimetric analysis with mass spectral analysis
- Differential scanning calorimetry
- Potentiometric surface acid/base titration, proton binding isotherms, and proton affinity distributions
- Ambient pressure STM/AFM
- Catalytic reactor; gas chromatographic and mass spectrometric product detection.
- TPO, TPR, TPD, pulsed chemisorption
- Pulsed catalytic reactor; rapid FTIR/ continuous product analysis
- Specialized reactors may be arranged*
- High pressure flow reactor, (up to 1500 psi and T to 600 C). optimized for oxidative dehydrogenation. (Contact: C. Narula)
- Ambient flow reactor for NOx catalysts, NOx traps and 3-way catalyst. Simulated vehicle exhaust, lean/rich swings, behavior.
- Ex-situ pre-treatment for TEM studies

Examples of Catalytic Evaluation and Characterization

Imaging Molecules, Active Sites, and Reactions on Nanocatalysts With STM

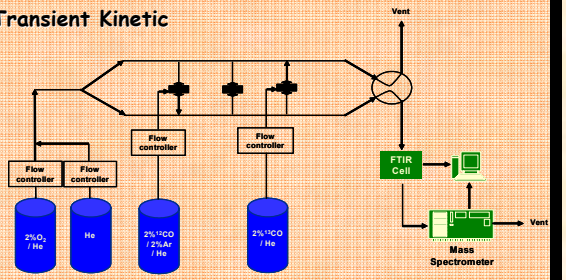
- Atomic resolution of surfaces
- Individual defects and ad-atoms
- Interpretation of image requires care



Pulsed Catalytic Reactor: Rapid FTIR/ Continuous Product Analysis

Use for Steady-State Isotopic-Transient Kinetic Analysis **(SSITKA)** - Advantages

- To determine *in situ* kinetic information about the reaction mechanism and the catalyst-surface reaction intermediates.
- Detection of isotopic labels in the reactor effluent species versus time following a switch (step change) in the isotopic labeling of one of the reactant species in the reactor feed.



- From isotopic transients of products, steady state kinetic parameters, such as the concentration of reactive intermediates (*Ni*) and the mean surface residence time (*ti*) are determined at actual reaction conditions.

SNS Facility and Catalysis

Applications in Catalysis : *in situ studies*

Neutrons are non-destructive and samples can be contained in stainless steel and quartz cells without penalty or usual difficulties associated with fluorescence

The Vision – Neutron Vibrational Spectrometer
Leader: J.Z. Larese
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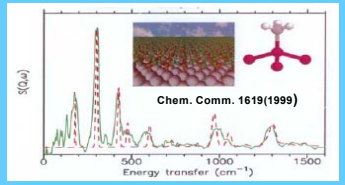
The Nanoscale-Ordered Materials Diffractometer (NOMAD)
Leader: J. Michael Simonson
simonsonjm@ornl.gov

- Local disorder in crystalline materials
- Dynamics of reactions and transformation of adsorbed species on heterogeneous catalysts
- Catalytic mechanisms
- Catalyst deactivation / poisoning and reaction intermediates.

Example:
Observed (solid line recorded at 20K) and calculated spectra from an industrial palladium catalyst after reaction.
The surface is covered with methyl groups (shown schematically in inset) which explains the deactivation



Theory/Modeling/Simulation and Catalysis

Contact: Thomas Schulthless schulthelesstc@ornl.gov
Peter Cummings cummingspt@ornl.gov

- Ab-initio computation of adsorbate and surface energetics
- Dynamics of reactions, transition states
- Simulation of reactor behavior at all length scales

Nanoscale Ordered MAterials Diffractometer (NOMAD)

Instrument development team: Mike Simonson (ORNL), Michael Winokur (Univ. Wisc.)
Instrument scientist: Jörg Neuefeind
Lead engineer: Kenneth Chipley

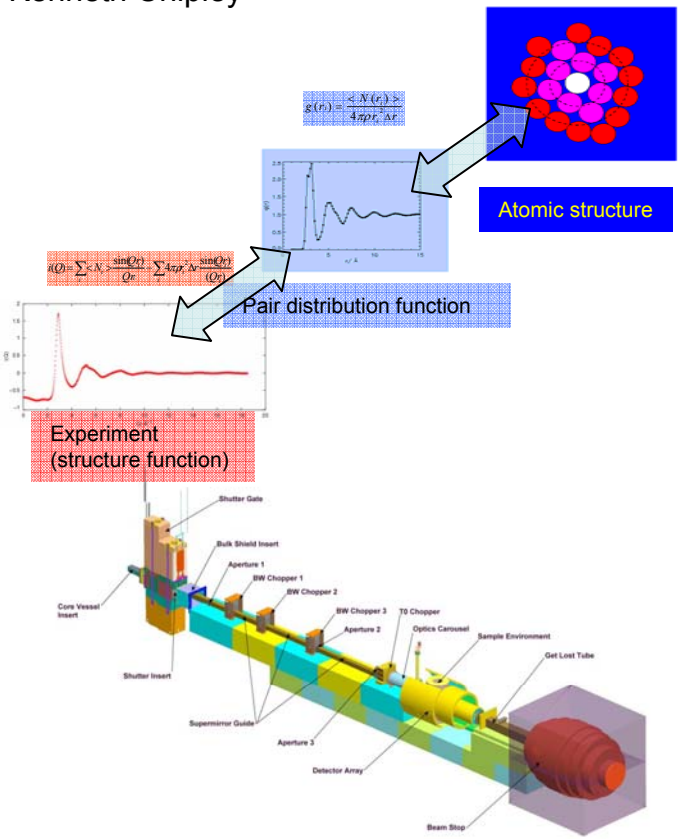
NOMAD is a high flux, medium resolution diffractometer using a large bandwidth of neutron energies and extensive detector coverage to do structural determination of local order in crystalline and amorphous materials. This instrument will enable studies of a large variety of samples ranging from liquids, solutions, glasses, nanocrystalline materials to long range ordered crystals. It will allow unprecedented access to high resolution pair distribution functions, small contrast isotope substitution experiments, small sample sizes and parametric studies

Possible experiments:

- Influence of the solvent (environment) on the structure of nanocrystalline materials
- In-situ structural changes in nanoscale oxide catalysts
- Local order in superconducting cuprates
- Low contrast isotope substitution experiments, e.g. $^{12}C/\ ^{13}C$ and $^{28}Si/\ ^{29}Si$ (Carbon based nanostructures)
- Micelle formation in supercritical CO_2
- Nanoscale confined liquids
- Resonant neutron scattering

Characteristics:

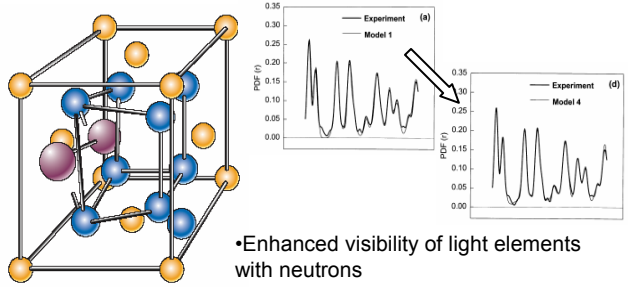
- High intensity
- High stability, low background
- Flexibility in resolution/intensity trade-off
- Large accessible momentum transfer range
- Continuous detector coverage



NOMAD diffractometer at SNS:
Anticipated completion date 2010
(Current opportunities exist at IPNS, LANSCE, ISIS, ILL…)

Examples:

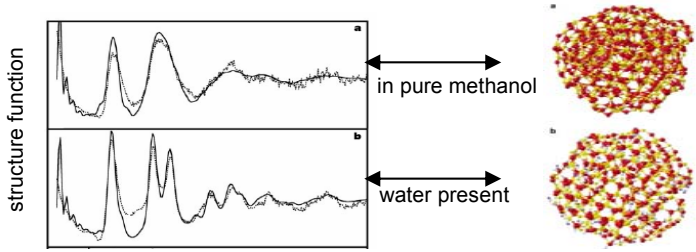
Oxygen in CeO_2 nanoparticles used in automobile catalytic converters



- Enhanced visibility of light elements with neutrons
- Statistical accuracy limits structural details discernible.

E. Mamontov, T. Egami: J. Phys. Chem. Sol. **61** (2000) 1345
(left figure: Nature **414** (2001) 332)

Water driven structure transformation in nanoparticles



X-ray experiment; with neutrons: isotope substitution (elements specific information)

H. Zhang, B. Gilbert, F. Huang and J. Banfield: Nature **424** (2003) 1025